

THERMAL DIFFUSION AND INTERMOLECULAR FORCES IN BINARY INERT GAS MIXTURES

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ABSTRACT. Thermal diffusion factors of the binary inert gas mixtures He-Ne, Ne-Kr and He-Kr have been measured by the two-bulb method. Some improvements over the previous methods of measurements have been made. The data have been utilised to obtain several significant results on the unlike interactions between these gas pairs.

INTRODUCTION

It is wellknown that of all the transport properties, thermal diffusion is most sensitive to the form of the intermolecular potential. The effect of inelastic collisions on thermal diffusion in polyatomic gases cannot as yet be predicted satisfactorily (Monchick *et al*, 1963). Consequently, for the determination of intermolecular potential from thermal diffusion data only mixtures of monatomic gases are suitable. The existing data on thermal diffusion in binary mixtures have recently been reviewed by Saxena and Mathur (1965). Even for monatomic gas mixtures, the existing data are not very consistent amongst themselves. The earlier measurements on thermal diffusion factor α in monatomic gases are those of Grew *et al* (1947, 1954) who have considered the temperature dependence of α , whereas, Atkins *et al* (1939) have considered the composition dependence. More recently Heymann and Kistemaker (1959), Grew and Mundy (1961) and Ghozlan (1963) have measured thermal diffusion factors in several binary gas mixtures by using tracer technique. In the measurements of Grew *et al* (1947, 1954) and Atkins *et al* (1939) thermal conductivity analyser was used for the purpose of gas analysis which is not capable of yielding very accurate data. Another difficulty which is also common to the more recent measurements using tracer technique is the large difference between the temperature of the lower and the upper bulbs which makes the temperature assignment somewhat uncertain. Saxena and Mathur (1965) have pointed out the inadequacy of the existing data and have also suggested that at least for systems containing He, the main source of discrepancy between experimental and the calculated values of α is the choice of the potential. Consequently, we have thought it desirable to measure thermal diffusion in some selected inert gas mixtures by making improvements in the method of measurements.

In this paper we have reported the measurement of α of He-Ne, Ne-Kr and He-Kr systems by a two-bulb method in the temperature range 340°-540°K. The

temperature dependence of α of these systems has been studied only by Grew *et al.*, (1947, 1954). For the systems He-Ne the ionization potentials of the components are not very different as distinct from the system He-Kr. The usual combination rules are based on equality of the ionization potential of the interacting molecules (Hirschfelder *et al.*, 1954). These studies are, therefore, expected to show whether the discrepancy between the experimental and the calculated values of α is mainly due to inadequacy of the combination rules for unlike interactions or due to the choice of the potential model.

EXPERIMENTAL

The apparatus consisted of two copper bulbs joined by a brass tube of 0.6 cm. diameter and a metal stopcock having a bore of the same dimension. The volume of the upper bulb was 943 cc and that of the lower bulb 65 cc. The use of copper bulbs ensures better temperature equilibration of the gases inside with the temperature of the surrounding medium. The bulbs were kept in two furnaces the temperature of which were controlled by electronic regulators. The temperature control of both the furnaces was within 1% of the temperature. The actual temperatures of the bulbs were measured by thermocouples. For analysis the bulbs were connected to suitable glass circuits and the analyses were made by a mass spectrometer (Associated Electrical Industries, MS3 model). The gases were supplied by Messrs British Oxygen Co., England. He and Ne were spectroscopically pure and Kr contained small amount of Xe as impurity.

The temperature assignment was made by the following usual formula

$$\bar{T} = \frac{T_H T_C}{T_H - T_C} \ln \frac{T_H}{T_C} \quad \dots (1)$$

where T_H and T_C are the temperatures of the upper and the lower bulb respectively. As an improvement over the previous methods we have varied both T_H and T_C so that the difference between them is not more than 100°C. This ensures that the formula for calculating \bar{T} should hold reasonably well. The relaxation time for the binary system was calculated from the equation (Saxena *et al.*, 1962).

$$\tau = \frac{L}{A} \left(\frac{T_1}{V_1} + \frac{T_2}{V_2} \right)^{-1} \left[\frac{T}{D} \right]_{AV} \quad \dots (2)$$

$$\left[\frac{T}{D} \right]_{AV} = \frac{1}{L} \int_0^L \frac{T}{D} \cdot dz$$

where L is the effective length of the tube, A is the cross-sectional area of the connecting tube, T_1 and T_2 the temperatures of the bulbs in °K and V_1 , V_2 the

corresponding volumes, T is some average temperature between T_1 and T_2 and D is the mutual diffusion coefficient at temperature T .

From the calculated relaxation times the time needed for attaining steady state for each system was estimated. After sufficient time was allowed for the steady state, the metal stop-cock was closed and samples were taken from the top and the bottom bulbs several times and the average of those were taken as the correct composition. The fact that gases in both the top and the bottom bulbs can be analysed in a mass spectrometer is an added advantage over the tracer technique where the counting probe is placed at the lower bulb only.

Thermal diffusion factor was then calculated from the equation,

$$\alpha = \frac{\ln q}{\ln T_H/T_C} \quad \dots (3)$$

where q is the separation factor given by,

$$q = \frac{(x_1/x_2)_{Top}}{(x_1/x_2)_{Bottom}} \quad \dots (4)$$

x_1, x_2 being the concentrations of the lighter and the heavier component respectively. The experimental values of α are shown in Table I. The average deviation

TABLE I
Experimental thermal diffusion factors and unlike interaction parameters

System	T	α	Unlike interaction parameters on L-J (12 : 6) potential			
			From experimental α		from combination rules	
			σ_{12} Å	$\epsilon_{12/k}$ °K	σ_{12} Å	$\epsilon_{12/k}$ °K
He-Kr (He = 92.5%)	380	.685	3.180	125.0	3.117	41.31
	420	.750				
	450	.785				
	490	.810				
	540	.830				
Ne-Kr (Ne = 95%)	339	.380	3.230	130.0	3.214	77.09
	378	.440				
	414	.465				
	454	.485				
	492	.500				
He-Ne (He = 21%)	532	.505				
	339	.260	—	—	2.652	19.07
	391	.285				
	426	.290				
	462	.290				
	496	.300				
	540	.310				

of q values was within 1%. Depending on the sensitivity of the logarithmic table the error in α values can be much larger. However, from the scatter of α values it appears that the error in our measured values should be within 5% and for the smoothed out values it should be much less. The thermal diffusion factors obtained by us are given in Table I.

As the compositions of our mixtures are quite different from those of Grew *et al* (1947, 1954) no direct comparison of our data is possible. For the system He-Kr it is possible to convert our data (7% of Kr) so that a comparison with data of Ghozlan (1963) (using Kr⁸⁵ as trace) is possible. Our α values are found to be systematically lower than those of Ghozlan (1963). It is relevant here to mention that Mason, Islam and Weissman (1964) observed a similar discrepancy with the data of Ghozlan (1963) for the H₂-Kr system. Consequently, it is likely that there is a systematic error in the measurements of Ghozlan.

COMPARISON WITH THEORY

In order to test whether the usually observed discrepancy between experimental and calculated values of α is due to the choice of the potential model we have considered the most commonly used potential energy functions viz (1) Lennard-Jones (12 : 6), (2) exp-6 and (3) core potential. These potentials can be written as follows :

1. Lennard-Jones (12:6) potential,

$$\phi(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] \quad \dots (5)$$

where r is the distance between the molecules, ϵ the depth of the potential well and σ is the value of r for which $\phi(r) = 0$.

2. Exp-6 potential :

$$\begin{aligned} \phi(r) &= \frac{\epsilon}{1 - \frac{6}{\alpha}} \left[\frac{6}{\alpha} \exp \left\{ \alpha - \left(1 - \frac{r}{r_m} \right) \right\} - \left(\frac{r_m}{r} \right)^6 \right] \quad r \geq r_{max} \\ &= \infty \quad r \leq r_{max} \quad \dots (6) \end{aligned}$$

where r_m is the value of r for which $\phi(r)$ is minimum and α is a parameter.

3. Core potential :

$$\begin{aligned} \phi(r) &= 4\epsilon \left[\left(\frac{\sigma - 2a}{r - 2a} \right)^{12} - \left(\frac{\sigma - 2a}{r - 2a} \right)^6 \right] \quad r > 2a \\ &= \infty \quad r \leq 2a. \quad \dots (7) \end{aligned}$$

where

σ is the value of r for which $\phi(r) = 0$.

ϵ is the depth of the potential well.

$2a$ is diameter of the spherical core.

Also

$$a^* = \frac{2a}{\sigma - 2a} \quad \text{and} \quad \frac{1}{\sigma - 2a} = 1 + \frac{1}{\sigma - 2a}$$

The force parameters for the different potential models used to calculate α are shown in Table II. For the Lennard-Jones (12:6) and exp-6 potentials the unlike interactions were approximated by the usual combination rules. For the

TABLE II

Force constants used for $L-J$ (12:6), exp-6, Kihara-core potential

	*L-J (12: 6)		*Exp-6			**Kihara-core potential		
	$\sigma \text{\AA}$	$\epsilon/k^\circ\text{K}$	$r_m \text{\AA}$	$\epsilon/k^\circ\text{K}$	α	$\sigma \text{\AA}$	$\epsilon/k^\circ\text{K}$	γ
He	2.556	10.22	3.135	9.16	12.4	2.313	41.3	0
Ne	2.749	35.60	3.147	38.0	14.5	2.673	52.5	0.05
Kr	3.679	167.00	4.956	158.3	12.3	3.570	204.0	0.11

* from Saxena *et al* (1965) **from Roy *et al* (1966)

core potential σ_{12} and ϵ_{12} were calculated by the combination rules used for the Lennard-Jones (12 : 6) potential and a_{12}^* were obtained from the relation,

$$(1 - a_{12}^*)^6 = [(1 - a_1^*)^6 \sigma_1^6 \times (1 - a_2^*)^6 \sigma_2^6]^{\frac{1}{2}} \quad (8)$$

The system He-Kr (with small percentage of Kr) may be considered as quasi-Lorentzian mixture and the Kihara approximation was used to calculate α (Hirschfelder *et al*, 1954). For the other two systems the Chapman-Cowling first approximation was used (Hirschfelder *et al*, 1954). The experimental and the calculated values of α for the different potentials are shown in Figs. 1-3. The collision integrals required for calculating α were obtained from MTGL by Hirschfelder *et al*. (1954) and those tabulated for the core potential by Barker (1964). As for He and Ne the core should be very small we have not calculated for the He-Ne system on the core potential. For the system He-Ne the agreement between the experimental and the calculated values of α is reasonably good. For the system Ne-Kr the agreement between the experimental and the calculated values is nearly the same for the Lennard-Jones (12 : 6) and the core potential but much worse for the exp-6 potential. It may also be seen that the slope of the experimental curve is steeper than that of the calculated curves. Regarding the system He-Kr

the same conclusions are similar to those for Ne-Kr although the difference between the experimental and the calculated values of α is more pronounced. It may also be seen that for this system core potential is slightly better than the Lennard-

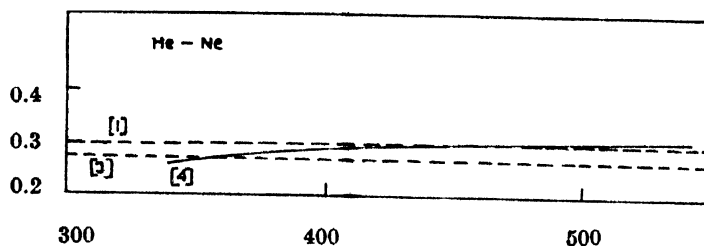


Fig. 1. Theoretical and Experimental curves for the thermal diffusion factor α of the system He-Ne.

- 1 Lennard-Jones (12 : 6)
- 3 Exp-six
- 4 Experimental.

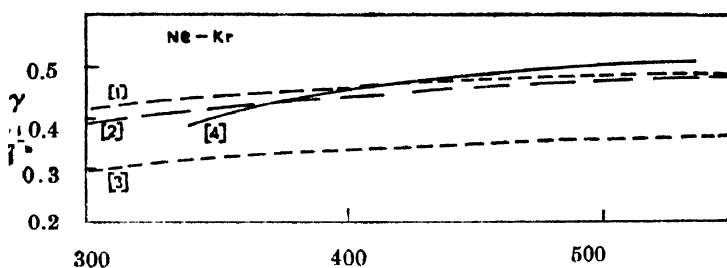


Fig. 2. Theoretical and experimental curves for the thermal diffusion factor α of the system Ne-Kr.

- 1 Lennard-Jones (12 : 6)
- 2 Kihara core.
- 3 Exp-six.
- 4 Experimental.

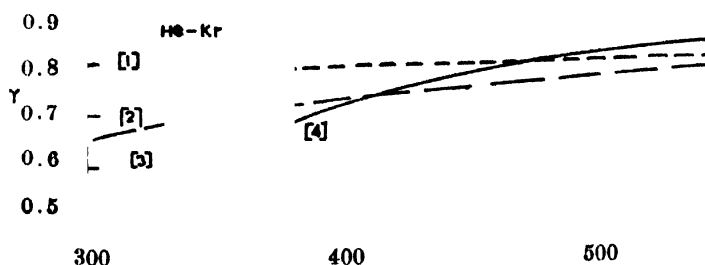


Fig. 3. Theoretical and experimental curves for the thermal diffusion factor α of the system He-Kr.

- 1 Lennard-Jones (12 : 6)
- 2 Kihara core.
- 3 Exp-six.
- 4 Experimental.

Jones (12 : 6) potential. One important result which comes out from these is that more different the constituents of the binary systems are the worse is the agreement between the experimental and the calculated values. It may be pointed out that the combination rule for ϵ (which is most important for calculating the temperature dependence of α) is based on the equality of the ionization potential for the interacting molecules (Hirschfelder *et al*, 1954). Consequently for dissimilar molecules the combination rule is likely to give erroneous results. It may also be seen that in contradiction to the suggestion of Saxena and Mathur (1965) the exp-6 potential fares worse than the Lennard-Jones (12: 6) potential for the He-Ne and very prominently for the He-Kr system.

DETERMINATION OF UNLIKE INTERACTIONS

It has been discussed above that the main source of discrepancy between the experimental and the calculated values of α probably lies in the combination rules. Consequently, we have thought it sufficient to determine the parameters for the Lennard-Jones (12: 6) potential only. Since for the system He-Ne the agreement with the calculated values is good we considered only the systems He-Kr and Ne-Kr.

The thermal diffusion factor to the first approximation can be written as (Hirschfelder *et al*, 1954).

$$\alpha_1 = A(6C_{12}^* - 5) \quad \dots (9)$$

where A is dependent on mole-fractions and potential parameters and C_{12}^* is a ratio of collision integrals which has been tabulated. A is a very slowly varying function of temperature. The second approximation to α can be written as,

$$\alpha_2 = A(6C_{12}^* - 5)(1+k) \quad (10)$$

where k is a correction term. For α values at two temperatures, T_1 and T_2 we have,

$$\frac{[\alpha_2]_{T_1}}{[\alpha_2]_{T_2}} = \frac{A_{T_1}}{A_{T_2}} \cdot \frac{\{6C_{12}^*(T_1) - 5\}}{\{6C_{12}^*(T_2) - 5\}} \cdot \frac{(1+k_{T_1})}{(1+k_{T_2})} \quad (11)$$

The variation of the correction term with temperature is very small so that we may write

$$\frac{[\alpha_2]_{T_1}}{[\alpha_2]_{T_2}} = \frac{A_{T_1}}{A_{T_2}} \cdot \frac{[6C_{12}^*(T_1) - 5]}{[6C_{12}^*(T_2) - 5]} \quad (12)$$

Since A is also a slowly varying function of temperature we have calculated AT_1 and AT_2 by the usual combination rules. Then from any pair of α values at two temperatures it is possible to calculate $\epsilon_{12/k}$ values from Eq. (12). Then as a second approximation this value of $\epsilon_{12/k}$ was used to calculate AT_1 and AT_2 .

and ϵ_{12}/k was determined again. Generally the difference between those values of ϵ_{12}/k was quite small. The average ϵ_{12}/k as determined from different pairs of α was taken as the correct value.

Once ϵ_{12}/k is known, σ_{12} can be obtained from the relation,

$$\alpha_2 = \alpha_1(1+k),$$

k may be written approximately as, (Weissman *et al.*, 1960)

$$k = \frac{1}{42} (8E_{22}^* - 7)^2 + \frac{2}{21} \left(1 - \frac{M_2}{M_1}\right) (8E_{22}^* - 7) [1 - \frac{3}{4}(5 - 4B_{12}^*)(6C_{12}^* - 5)^{-1}] \quad (13)$$

where

$$B_{12}^* = \frac{5\Omega_{12}^{(1,2)*} - 4\Omega_{12}^{(1,1)*}}{\Omega_{12}^{(1,1)*}}$$

and
$$E_{22}^* = \frac{\Omega_{22}^{(2,2)*}}{\Omega_{22}^{(2,1)*}}$$

the subscript 1 refers to the heavier species. From Eq. (10) it is possible to find the value of σ_{12} which represents α_2 correctly. The average of σ_{12} as determined from α values at different temperatures was taken as the correct value. The parameters thus obtained are shown in Table I together with those calculated from the combination rules.

It may be seen from the Table I that the depth of the potential well for the unlike interactions is much deeper than that given by the combination rule. It appears that the heavier molecule predominates in the interaction and equal weight cannot be placed on two dissimilar molecules to calculate the unlike interaction parameters.

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